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# JAPAN KOKAI TOKKYO KOHO

ARP-66

**H8-269030 (1996)**

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(54) [Title of the Invention]

## METHOD FOR PREPARING PROPYLENE OXIDE

(57) [Abstract]

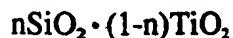
[Purpose] To provide a method for preparing propylene oxide in high selectivity.

[Constitution] In a method for preparing propylene oxide by direct oxidation of propylene with oxygen and hydrogen, the reaction temperature is made to 0-40°C in said direct oxidation reaction of propylene with oxygen and hydrogen in the presence of catalysts given by supporting noble metals of Group VIII in the periodic table on titanosilicates.

[Claims]

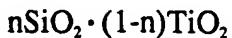
[Claim 1] A method for preparing propylene oxide, characterized by that the reaction temperature is made to 0-40°C in a method for preparing propylene oxide by the direct oxidation of propylene with oxygen and hydrogen in the presence of catalysts given by supporting noble metals of Group VIII in the periodic table on titanosilicates.

[Claim 2] The method for preparing propylene oxide described in Claim 1, characterized by that titanosilicates being a synthetic zeolite material which is represented by the following general formula



(where  $n = 0.8-0.999$ ) and shows an X-ray diffraction pattern of pentasil (ペントシリ) structure are used as said titanosilicates.

**[Claim 3]** The method for preparing propylene oxide described in Claim 1, characterized by that titanosilicates being a synthetic zeolite material which is represented by the following general formula



(where  $n = 0.8-0.99$ ), shows an X-ray diffraction pattern of MFI structure, shows an absorption around  $960 \text{ cm}^{-1}$  in the infrared spectra and has fine pores of  $10-20 \text{ \AA}$  that are different from fine pores of  $5-6 \text{ \AA}$  originally possessed by said MFI zeolite, are used as said titanosilicates.

**[Claim 4]** The method for preparing propylene oxide described in Claim 1, characterized by that titanosilicates which are synthesized by mixing a tetraalkyl orthosilicate, a tetraalkyl orthotitanate and an aqueous solution of tetraalkylammonium hydroxide so that they become the following ratios

$$\text{SiO}_2/\text{TiO}_2 = 1.0-7.0$$

$$\text{RN}^+/\text{SiO}_2 = 0.1-1.0$$

(where  $\text{RN}^+$  indicates a tetraalkylammonium hydroxide)

$$\text{H}_2\text{O/SiO}_2 = 10-100,$$

and making hydrothermal synthesis of this mixture at temperatures of  $100-250^\circ\text{C}$  for 30 min - 5 days, are used as said titanosilicates.

### **[Detailed Explanation of the Invention]**

#### **[0001]**

**[Fields of Industrial Application]** This invention is related to a novel method for preparing propylene oxide. The propylene oxide obtained by this invention is a very useful compound for a raw material of propylene glycol or polypropylene glycol, etc.

#### **[0002]**

**[Previous Art]** The chlorohydrin method from propylene via chlorohydrin has been known as a method for preparing propylene oxide. The Halcon method for oxidizing propylene with t-butyl hydroperoxide or ethylbenzene hydroperoxide as oxidizing agent and the peracetic acid method with peracetic acid as oxidizing agent have also been known.

**[0003]** However, a two-step or higher process from propylene becomes necessary in aforesaid chlorohydrin method. Because chlorohydrin is dehydrochlorinated with lime milk, a large quantity

of calcium chloride is by-produced, thus the treatment of this by-product becomes a problem. A process for preparing oxidizing agent is necessary to be arranged with the Halcon method or peracetic acid method, t-butanol and acetic acid are concurrently produced, thus the market guarantee of these concurrent products is needed.

[0004] In the methods for preparing propylene oxide, for this reason, several attempts have been made which are processes requiring no treatment of by-products and no market guarantee of concurrent products, and give propylene oxide from propylene in one step.

[0005] For example, a method for direct oxidation of propylene with oxygen and hydrogen using titanosilicates as catalyst has been disclosed in Japan Kokai S59-51273 (1984).

[0006] A method for preparing propylene oxide by direct oxidation reaction of propylene with oxygen and hydrogen using catalysts comprising noble metals of Group VIII in the periodic table and titanosilicates has been disclosed in Japan Kokai H4-352771 (1992).

[0007]

**[Subjects to Be Solved by the Invention]** However, more than equimolar expensive hydrogen peroxide to form propylene oxide was needed in the method described in Japan Kokai S59-51273 (1984), thus the method had a problem with economy.

[0008] The method described in Japan Kokai H4-352771 (1992) was excellent in no use of expensive hydrogen peroxide, but the selectivity of propylene oxide varied with the composition of raw gas during oxidation reaction and preparing conditions of catalyst, etc., thus this method was not sufficient for an industrial production method.

[0009] This invention is made in view of aforesaid subjects, and its purpose is to provide a method for preparing propylene oxide in high selectivity and without aforesaid problems in the direct oxidation reaction of propylene with oxygen and hydrogen.

[0010]

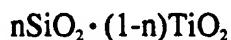
**[Means for Solving the Subjects]** The inventors made earnest investigations on a method for preparing propylene oxide. As a result, they discovered that in a method for preparing propylene oxide by the direct oxidation of propylene with oxygen and hydrogen in the presence of catalysts given by supporting noble metals of Group VIII in the periodic table on titanosilicates, if the reaction is conducted in a specific range of reaction temperature, propylene oxide can be obtained in high selectivity and without affects of raw gas composition and preparing conditions of catalyst, thus came to accomplish this invention.

[0011] Namely, this invention is a method for preparing propylene oxide, characterized by that the reaction temperature is made to 0-40°C in the direct oxidation of propylene with oxygen and hydrogen in the presence of catalysts given by supporting noble metals of Group VIII in the periodic table on titanosilicates.

[0012] Next, this invention is explained in more detail.

[0013] Catalysts given by supporting noble metals of Group VIII in the periodic table on titanosilicates are used in the invented method.

[0014] The titanosilicates mentioned in this invention mean titanosilicates being a synthetic zeolite material which is represented by the following general formula,



shows an X-ray diffraction pattern of pentasil structure, and in which a part of silicon atoms forming crystal lattice of crystalline  $\text{SiO}_2$  (called silicalite) with zeolite structure are substituted by titanium atoms. In the general formula, n is commonly 0.8-0.999.

[0015] The synthetic methods of titanosilicates used in this invention are not specially restricted, and they may be synthesized by well-known methods, for instance, methods given in Japan Kokai S56-96720 (1981) or Japan Kokai S60-127217 (1985).

[0016] According to Japan Kokai S56-96720 (1981), the titanosilicates are synthesized by hydrolysis of a tetraalkyl orthosilicate and a tetraalkyl orthotitanate with an aqueous solution of tetraalkylammonium hydroxide, and then hydrothermal synthesis.

[0017] In this invention, the tetraalkyl orthosilicates are not specially restricted, for instance, tetramethyl orthosilicate, tetraethyl orthosilicate, tetrapropyl orthosilicate, tetrabutyl orthosilicate, tetrapentyl orthosilicate, tetrahexyl orthosilicate, tetraheptyl orthosilicate, tetraoctyl orthosilicate, trimethylethyl silicate, dimethyldiethyl silicate, methyltriethyl silicate, dimethyldipropyl silicate, and ethyltripropyl silicate, etc. are given. Tetraethyl orthosilicate is preferably used among them from the ease of availability.

[0018] The tetraalkyl orthotitanates are not specially restricted, for instance, tetramethyl orthotitanate, tetraethyl orthotitanate, tetrapropyl orthotitanate, tetrabutyl orthotitanate, tetraoctyl orthotitanate, trimethylethyl titanate, dimethyldiethyl titanate, methyltriethyl titanate, dimethyldipropyl titanate, and ethyltripropyl titanate, etc. are given. Tetraethyl orthotitanate and tetrabutyl orthotitanate are preferably used among them from the ease of availability.

[0019] The tetraalkylammonium hydroxides are not specially restricted, for instance, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, etc. are given. Tetrapropylammonium hydroxide is preferably used among them from the ease of availability.

[0020] The charge ratios of these raw materials in synthesizing titanosilicates are not specially restricted, but it is preferable to do as follows. The amount of tetraalkyl orthosilicates is 1-100 eq to 1 mol tetraalkyl orthotitanate, preferably 5-35 eq. The amount of tetraalkylammonium hydroxide is 0.1-1 eq to 1 mol tetraalkyl orthosilicate, preferably 0.2-0.6 eq. Moreover, the concentration of aqueous tetraalkylammonium hydroxide solutions is commonly 3-50 wt%, preferably 5-40 wt%.

[0021] In this invention, the hydrolysis temperature in synthesizing the titanosilicates is not specially restricted, commonly -20 - 60°C, preferably -10 - 40°C. The reaction time is not specially restricted, commonly 10 min - 100 hr, preferably 30 min - 50 hr. Solvents can be used during hydrolysis if necessary. The solvents are not specially restricted, for instance, alcohols such as methanol, ethanol, propanol, butanol, octanol, etc.; ketones such as acetone, methyl ethyl ketone, etc.; ethers such as diethyl ether, tetrahydrofuran, dimethoxyethane, etc., can be given.

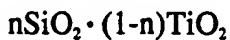
[0022] In the hydrolysis, the mixing order and mixing method of reactants tetraalkyl orthosilicate, tetraalkyl orthotitanate and aqueous tetraalkylammonium hydroxide are not specially restricted if uniform hydrolysis products are obtained. For instance, all aforesaid compounds may be mixed at a time, or an aqueous tetraalkylammonium hydroxide solution may be dropped into a mixture of tetraalkyl orthosilicate and tetraalkyl orthotitanate. Moreover, an aqueous tetraalkylammonium hydrochloride solution may be added into tetraalkyl orthosilicate and then a tetraalkyl orthotitanate is added. By-produced alcohol is not necessarily removed, but its quantity is preferably decreased by heating in advance.

[0023] Water is added into the hydrolysis product obtained as above according to demand, and the mixture is delivered to hydrothermal synthesis. The water amount used for the hydrothermal synthesis is adjusted so that the sum of this water and water added during hydrolysis is commonly 15-100 eq. to 1 mol silicon atom, preferably becomes 25-80 eq. The hydrothermal synthesis reaction is commonly carried out by heating this mixed solution in a closed vessel

under temperature condition of commonly 60-300°C, preferably 100-200°C and keeping this temperature for 1-100 hr, preferably 6-50 hr. At this time, the pressure can be applied either by self-pressurization or pressurization, and commonly by self-pressurization. The stirring of reaction system is not necessarily conducted, and the crystallization fully proceeds even if the system is in a state of stand still.

[0024] The solid powder thus treated and crystallized by hydrothermal synthesis is fully washed with ion exchanged water and then delivered to calcination, The calcination temperature is commonly 300-700°C, preferably 350-600°C. The calcination time is not specially restricted, but titanosilicates can be prepared by making calcination commonly for 1-50 hr, preferably 2-20 hr.

[0025] The titanosilicates being a synthetic zeolite material which is represented by the following general formula



(where  $n = 0.8-0.99$ ), shows an X-ray diffraction pattern of MFI structure, shows an absorption around 960  $\text{cm}^{-1}$  in the infrared absorption spectra and have fine pores of 10-20 Å that are different from fine pores of 5-6 Å originally possessed by said MFI zeolite, can be used as the titanosilicates in this invention.

[0026] Because aforesaid titanosilicates are titanosilicates having the MFI structure rich in heat stability and having fine pores of 10-20 Å that are different from fine pores of 5-6 Å originally possessed by said MFI zeolite, they are not affected by diffusion control, have high catalyst activity for compounds with relatively large molecular size and suitable for the titanosilicates of this invention.

[0027] Aforesaid titanosilicates are synthesized by mixing a tetraalkyl orthosilicate, a tetraalkyl orthotitanate and an aqueous solution of tetraalkylammonium hydroxide so that they become the following ratios

$$\text{SiO}_2/\text{TiO}_2 = 1.0-7.0$$

$$\text{RN}^+/\text{SiO}_2 = 0.1-1.0$$

(where  $\text{RN}^+$  indicates a tetraalkylammonium hydroxide)

$$\text{H}_2\text{O/SiO}_2 = 10-100,$$

and making hydrothermal synthesis of this mixture at temperatures of 100-250°C for 30 min - 5 days.

[0028] If necessary, boron, aluminum, phosphorus, calcium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium or zirconium, etc. may also be contained in the titanosilicates used in this invention, and the titanosilicates containing different elements can be synthesized by adding oxide sources of these metals.

[0029] In this invention, the synthesized titanosilicates may be used as they are, or may be used by molding. When they are used by molding, binders are generally used. The type of binders is not specially restricted, for instance, silica, alumina, etc. are used.

[0030] In this invention, the noble metals of Group VIII in the periodic table supported on the titanosilicates are not specially restricted, for instance, ruthenium, rhodium, palladium, iridium, and platinum, etc. can be given. Palladium and platinum are preferable among them from the viewpoint of catalyst activity. Moreover, aforesaid noble metals not only can be used separately and individually, but may also be used by mixing 2 or more of them.

[0031] As the noble metal compounds that become raw materials of these noble metals, various inorganic compounds or organic compounds such as nitrates, sulfates, halides, inorganic complexes, organic acid salts, etc. can be used, inorganic complexes and halides are preferable among them. For instance, in case of palladium, inorganic salts such as palladium nitrate, palladium sulfate, etc., halides such as palladium chloride, inorganic complexes such as tetrammine palladous dichloride, etc., organic acid salts such as palladium acetate, etc. are given. Tetrammine palladous dichloride and palladium chloride are preferably used among them.

[0032] In this invention, methods for supporting the noble metals onto the titanosilicates are not specially restricted, and aforesaid raw materials can be used to support them by well-known methods such as impregnation method, precipitation method, blending method, sedimentation method, etc. The impregnation method is preferable among them from the ease of supporting method. Then aforesaid noble metal compounds supported on the titanosilicates are dried, and calcined if desired.

[0033] In this invention, the noble metals of Group VIII in the periodic table supported on the titanosilicates must be in a metallic state. Therefore, a reducing treatment is applied to aforesaid noble metals supported on the titanosilicates before use. This reducing treatment may be made in the catalyst preparation process or in the reaction system without troubles. These reduction methods are not specially restricted. When the reduction is conducted in the catalyst preparation

process, a wet reduction method conducted in solutions of sodium formate, formaldehyde, hydrazine, etc., or a dry reduction method conducted in a gas phase with reducing gases such as hydrogen, carbon monoxide, etc. diluted by inert gases such as nitrogen, helium, etc., can be used. When the reduction is conducted in an oxidation reaction system, the titanosilicates supporting noble metal compounds are suspended in solvents used for the oxidation reaction and aforesaid reducing gases may be circulated in these suspensions. These suspensions can become catalyst suspensions as they are, and the oxidation reaction can be started with the supply of raw gases.

[0034] The reducing treatment temperature of noble metal compounds is 0-500°C, preferably 5-160°C, and more preferably 10-90°C. If the reducing treatment temperature is lower than 0°C, the noble metal compounds are not fully reduced to a metallic state, and the catalyst activity essentially decreases. If the reducing treatment temperature is more than 500°C, on the other hand, the dispersibility of supported noble metals decreases, thus the selectivity of propylene oxide decreases. The reducing treatment time is not specially restricted if the reduction of noble metal compounds fully proceeds, and it is commonly 5 min - 24 hr.

[0035] The supported amount of aforesaid noble metals in this invention is commonly 0.01-10 wt%, preferably 0.05-5 wt% as metal to the total catalyst weight for improving reaction rate and economy.

[0036] The oxidation of this invention is conducted in a liquid phase, more specifically, by use of solvents. The solvents are not specially used, for instance, aliphatic alcohols such as methanol, ethanol, butanol, pentanol, hexanol, heptanol, and octanol, etc.; glycols such as ethylene glycol, propylene glycol, etc.; ethers such as dimethyl ether, diethyl ether, tetrahydrofuran, dimethoxyethane, etc.; glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, etc.; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, etc.; carboxylic acids such as acetic acid; or water, etc., are given. Water is preferable among them from the viewpoint of easy handling. Aforesaid solvents not only can be used separately and respectively, but also can be used by mixing two or more of them.

[0037] In this invention, the amount of noble metals of Group VIII in the periodic table supported on the titanosilicates varies with the reaction type. For instance, when the reaction is carried out by a fixed bed continuous circulating type, the amount is decided by the reaction rate and heat balance, thus is not specially restricted. When the reaction is carried out by a batch type, semi-batch type or continuous circulating type of suspension bed, the amount of catalyst is commonly 0.01-30 wt% to solvent, preferably 0.05-20 wt%. If the amount is more than this range, sometimes it makes a trouble with the stirring of catalyst suspension.

[0038] In the invented method, the reaction temperature during the direct oxidation of propylene with oxygen and hydrogen is 0-40°C, preferably 10-35°C for increasing the reaction rate and inhibiting side reactions. If the reaction temperature is lower than 0°C, the reaction rate decelerates, while the reaction temperature is higher than 40°C, side reactions tend to increase, thus the selectivity of propylene oxide decreases. The reaction pressure is commonly normal pressure - 200 kg/cm<sup>2</sup>, preferably normal pressure - 50 kg/cm<sup>2</sup>.

[0039] The propylene used in this invention may be either in a gas or liquid state. When it is in a liquid state, the reaction may be carried out under pressure.

[0040] It does not matter if propylene, oxygen and hydrogen gases supplied in this invention are diluted with inert gases such as nitrogen, helium, argon, carbon dioxide, and their mixed gases, etc. Atmospheric oxygen can also be used as oxygen. The oxygen supply varies with reaction methods and reaction conditions, thus is not restricted. The reaction is generally carried out at the oxygen supply of 0.01 mL/min - 1,000 mL/min, preferably 0.1 mL/min - 500mL/min per catalyst unit weight (g) to increase the productivity and conversion of oxygen. The ratios of raw gases are not specially restricted and can be optionally changed, but they are preferably taken as follows. The hydrogen/oxygen (mole ratio) is preferably 0.01-10, and the propylene/oxygen (mole ratio) is preferably 0.1-10.

[0041] The gas hourly space velocities (GHSV) of raw gases containing inert gases and catalyst are 1,000-50,000 hr<sup>-1</sup>, preferably 2,000-40,000 hr<sup>-1</sup>. Here GHSV designates the supply amount of propylene, oxygen, hydrogen and inert gases supplied at 20°C per unit time per unit catalyst volume.

[0042] In this invention, reaction methods are not specially restricted. Any of a batch type method wherein reacants propylene, oxygen, hydrogen, a catalyst and a solvent are charged into

a reaction apparatus at a time, a semi-batch type method wherein propylene oxide, oxygen and hydrogen are continuously blown into a reaction apparatus, and a fixed bed or suspension bed continuous type method wherein propylene oxide, oxygen and hydrogen are continuously supplied and unreacted gas and reaction liquid are continuously withdrawn, can be carried out.

[0043] The propylene oxide formed in this invention can be readily separated by well-known methods, such as sequential distillation, etc.

[0044]

[Examples] This invention is illustrated in more detail by examples. This invention is outlined by these examples, but not restricted to these examples.

[Example 1]

In a four-necked flask of 1,000 mL in inner volume equipped with a thermometer and a stirring device, 43.9 g tetraethyl orthotitanate and then 198 g tetraethyl orthosilicate were added and mixed in a nitrogen stream. This mixed solution was cooled to 0°C, then 347 g a 25 wt% aqueous solution of tetrapropylammonium hydroxide was dropped in 1 hr by using a feed pump, and stirred at room temperature for additional 1 hr to make mature treatment. The mixture became a homogeneous solution after stirring. Ethanol and water formed by the hydrolysis were distilled and removed by heating this four-necked flask around 90°C in an oil bath.

[0045] 596 g ion exchanged water was added into the mixture given by the distillation and removal, then 450 mL of it was put into a Hastelloy pressure-resistant reaction vessel of 500 mL in inner volume equipped with a thermometer and stirring device, raised to 170°C in 2 hr under self-pressurization, and stirred for 48 hr to conduct a hydrothermal synthesis. The content of autoclave was centrifugalized, and fully washed with ion exchange water of 65°C. The resulting white powder was dried at 90°C for 15 hr, and then calcined at 550°C for 5 hr to obtain 21.5 g a titanosilicate. The main peaks given by X-ray diffraction (XRD) and the intensity ratio of the peaks are shown in Table 1. This crystal structure indicated a MFI structure.

[0046] [Table 1]

Lattice Plane Distance (Å)	Diffracted Intensity Ratio (I/I <sub>max</sub> )
11.12	1.00
10.00	0.58
6.70	0.06
6.35	0.14
5.98	0.19
5.70	0.09
5.56	0.13
4.99	0.06
4.35	0.06
4.25	0.09
3.84	0.63
3.71	0.32
3.64	0.21
3.43	0.07
3.30	0.06
3.05	0.07
2.98	0.08
2.01	0.06

[0047] This titanosilicate shows a characteristic absorption around 960 cm<sup>-1</sup> by infrared absorption spectroscopic measurement (Fig. 1). Moreover, the fine pore distribution measured by N<sub>2</sub> adsorption indicates the existence of fine pores characteristic of 10-20 Å (Fig. 2).

[0048] An aqueous solution of tetraammine palladous (II) chloride was added into this titanosilicate so that the weight of palladium atom to titanosilicate became 0.5 wt%, then stirred and mixed at room temperature for 1 hr. This suspension was evaporated and dried out, and then reduced in gas phase at 150°C for 1 hr under the circulation of 17 vol% hydrogen diluted with nitrogen to obtain a Pd-supported titanosilicate catalyst.

[0049] In a normal pressure semi-batch glass reaction apparatus of 100 mL in inner volume equipped with a thermometer, a stirring device and a gas blow-in inlet, 0.5 g the Pd-supported titanosilicate as catalyst and 60 mL water as solvent were added and stirred. Here propylene, oxygen and hydrogen were fed at 30 mmol/hr, 80 mmol/hr, 20 mmol/hr and 303 mmol/hr, respectively and the temperature was kept at 45°C to carry out the epoxidation of propylene. The exit gas was introduced into a n-butane trap in an ice bath to collect accompanied propylene in the trap. The reaction product was analyzed by a gas chromatograph. The results of 11 hr after the reaction started are shown in Table 2.

$$C_J = 30 \text{ mmol/hr}^{12} \quad N_2 = 303 \text{ mmol/hr}$$

$$O_2 = 80 \text{ " /hr}$$

	Ex. 1	Ex. 2	Comp. Ex. 1	Ex. 3	Comp. Ex. 2	Ex. 4	Comp. Ex. 3	Comp. Ex. 4
Catalyst preparing conditions								
maturing time (hr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
hydrothermal synthesis time (hr)	48	48	48	48	48	48	48	48
H <sub>2</sub> O/Si ratio (mole ratio)	50	50	50	50	50	50	50	50
Reaction conditions								
reaction temperature (°C)	26	35	45	26	45	28	45	45
Raw gas supply (mmol/hr)								
propylene	30	30	30	30	30	30	30	30
oxygen	80	80	80	80	80	80	80	80
hydrogen	20	20	20	15	15	10	20	20
nitrogen	303	303	303	303	303	303	303	303
Conversion (mol %)	0.7	0.6 <sup>2</sup>	2.3	0.4	1.1	0.5	0.5	0.9
Product selectivity (mol %)								
propylene oxide	97.4	96.6	56.2	98.7	43.6	96.9	52.3	60.4
propane	1.1	2.5	43.4	0	55.2	3.1	47.2	38.7
acetone	1.4	0.9	0.4	1.3	1.2	0	0.5	0.9

Increasing T has a negative effect.

**[0051] [Example 2]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the reaction temperature was taken as 35°C. The results are shown together in Table 2.

**[0052] [Comparison Example 1]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the reaction temperature was taken as 45°C. The results are shown together in Table 2.

**[0053] [Example 2]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrogen supply was taken as 15 mmol/hr. The results are shown together in Table 2.

**[0054] [Comparison Example 2]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrogen supply was taken as 15 mmol/hr and the reaction temperature as 45°C. The results are shown together in Table 2.

**[0055] [Example 4]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrogen supply was taken as 10 mmol/hr. The results are shown together in Table 2.

**[0056] [Comparison Example 3]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrogen supply was taken as 10 mmol/hr and the reaction temperature as 45°C. The results are shown together in Table 2.

**[0057] [Comparison Example 4]**

The epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrogen supply was taken as 20 mmol/hr and the reaction temperature as 45°C. The results are shown together in Table 2.

**[0058] [Comparison Example 4]**

The Pd-supported titanosilicate was prepared and the epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrothermal synthesis time was taken as 6 hr. The results are shown together in Table 2.

Example 5?  
Table 3?

[0059]

[Table 3]

	Ex. 5	Comp. Ex. 5	Ex. 6	Ex. 7	Ex. 8
<b>Catalyst preparing conditions</b>					
maturing time (hr)	1.0	1.0	2.0	4.0	1.0
hydrothermal synthesis time (hr)	6	6	48	48	12
H <sub>2</sub> O/Si ratio (mole ratio)	50	50	50	50	30
<b>Reaction conditions</b>					
reaction temperature (°C)	26	45	26	26	26
<b>Raw gas supply (mmol/hr)</b>					
propylene	30	30	30	30	30
oxygen	80	80	80	80	80
hydrogen	20	20	20	20	20
nitrogen	303	303	303	303	303
<b>Conversion (mol%)</b>	0.9	1.8	0.8	0.5	0.7
<b>Product selectivity (mol%)</b>					
propylene oxide	80.7	35.5	99.4	95.5	90.7
propane	18.8	63.9	0.0	0.0	9.3
acetone	0.5	0.6	0.6	4.5	0.0

**[0060] [Comparison Example 5]**

The Pd-supported titanosilicate was prepared and the epoxidation of propylene was carried out in the same way as in Example 1 except that the hydrothermal synthesis time was taken as 6 hr, the oxygen supply as 20 mmol/hr and the reaction temperature as 45°C. The results are shown together in Table 3.

**[0061] [Example 6]**

The Pd-supported titanosilicate was prepared and the epoxidation of propylene was carried out in the same way as in Example 1 except that the maturing time was taken as 2 hr. The results are shown together in Table 3.

**[0062] [Example 7]**

The Pd-supported titanosilicate was prepared and the epoxidation of propylene was carried out in the same way as in Example 1 except that the maturing time was taken as 4 hr. The results are shown together in Table 3.

**[0063] [Example 8]**

In a four-necked flask of 1,000 mL in inner volume equipped with a thermometer and a stirring device, 44.8 g tetraethyl orthotitanate and then 195 g tetraethyl orthosilicate were added and mixed in a nitrogen stream. This mixed solution was kept at 20°C, then 346 g a 25 wt% aqueous solution of tetrapropylammonium hydroxide was dropped in 1 hr by using a feed pump, and stirred at room temperature for additional 1 hr to make mature treatment. Ethanol and water formed by the hydrolysis were distilled and removed (255 mL) by heating this four-necked flask around 90°C in an oil bath.

**[0064]** 250 g ion exchanged water was added into the mixture given by the distillation and removal, then 450 mL of it was put into a Hastelloy pressure-resistant reaction vessel of 500 mL in inner volume equipped with a thermometer and stirring device, raised to 170°C in 2 hr under self-pressurization, and stirred for 12 hr to conduct a hydrothermal synthesis. The content of autoclave was centrifugalized, and fully washed with ion exchange water of 65°C. The resulting white powder was dried at 90°C for 15 hr, and then calcined at 550°C for 5 hr to obtain 25.6 g a titanosilicate.

**[0065]** An aqueous solution of tetraammine palladous (II) chloride was added into this titanosilicate so that the weight of palladium atom to titanosilicate became 0.5 wt%, then stirred and

mixed at room temperature for 1 hr. This suspension was evaporated and dried out, and then reduced in gas phase at 150°C for 1 hr under the circulation of 17 vol% hydrogen diluted with nitrogen to obtain a Pd-supported titanosilicate catalyst. In a normal pressure semi-batch glass reaction apparatus of 100 mL in inner volume equipped with a thermometer, a stirring device and a gas blow-in inlet, 0.5 g the Pd-supported titanosilicate as catalyst and 60 mL water as solvent were added and stirred. Here propylene, oxygen and hydrogen were fed at 30 mmol/hr, 80 mmol/hr, 20 mmol/hr and 303 mmol/hr, respectively and the temperature was kept at 26°C to carried out the epoxidation of propylene. The results are shown together in Table 3.

**[0066]**

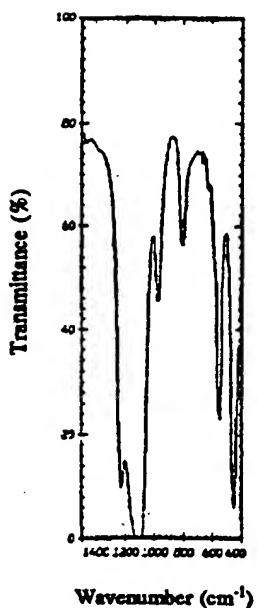
**[Effects of the Invention]** According to this invention, in the method for preparing propylene oxide by the direct oxidation reaction of propylene with oxygen and hydrogen in the presence of catalysts given by supporting noble metals of Group VIII in the periodic table on titanosilicates, propylene oxide can be prepared in high selectivity and without affectations of raw gas composition or preparing conditions of catalysts by making the reaction temperature to 0-40°C.

**[Simple Illustration of the Figures]**

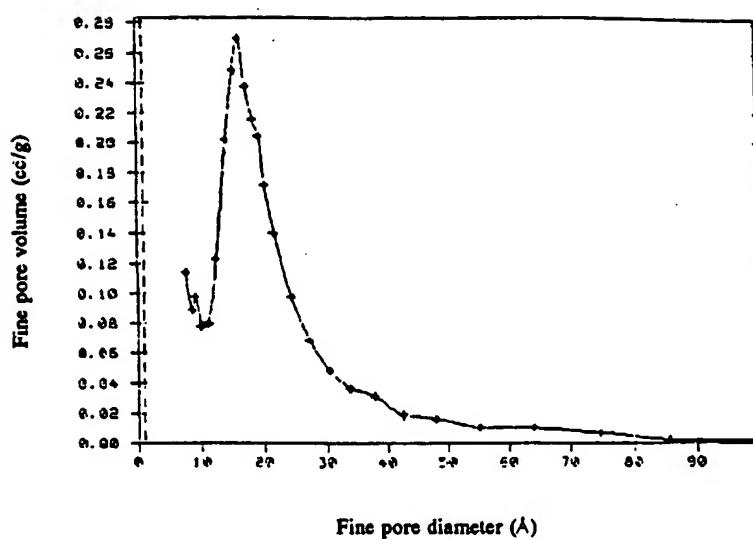
**[Figure 1]** A graph showing the infrared absorption spectrum of a titanosilicate having MFI structure and obtained by Example 1.

**[Figure 2]** A graph showing the fine pore distribution of a titanosilicate having MFI structure and obtained by Example 1.

[Fig. 1]



[Fig. 2]



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